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①⑨ ①CA **CANADIAN PATENT** ①②

⑤④ DIFFERENTIAL FROTH FLOTATION OF MOLYBDENUM  
SULFIDE FROM COPPER SULFIDE

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ABSTRACT OF THE DISCLOSURE

An improved process of differential froth flotation applied to a flotation pulp of molybdenite and copper sulfide using only a small amount of a water-soluble ammonium, alkali metal or alkaline earth metal sulfide compound as depressant with nitrogen aeration.

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#### FIELD OF THE INVENTION

10       The field of art to which the invention pertains includes the field of differential froth flotation, particularly with the employment of preferential modifying agents. More specifically, the field relates to the separation and recovery of molybdenum sulfide from copper ore concentrate containing both molybdenum sulfide and copper sulfide by froth flotation in the presence of a depressant for copper sulfide to effect recovery of a molybdenum concentrate in the flotation overflow and recovery of a copper concentrate in the flotation underflow.

#### BACKGROUND AND SUMMARY OF THE INVENTION

20       Molybdenite ( $\text{MoS}_2$ ) can be found in small amounts with sulfidic copper ores such as those containing chalcopyrite. Typically, copper ores of such nature are beneficiated by



flotation to obtain an ore concentrate containing about 25-30% copper and about 0.3-1% molybdenum. In obtaining the concentrate, reagents such as collectors and frothers are added during treatment of the ore to facilitate separation from the gangue materials, the molybdenite following the copper sulfide in the flotation circuit to obtain a concentrate as above described. Thereafter, the molybdenite content of the copper ore concentrate is separated by differential flotation to obtain a molybdenum concentrate containing about 40% or more Mo. In view of the fact that sulfidic copper minerals and molybdenite are floated by the same collectors, in order to effect a differential flotation of the molybdenite it has been found necessary to depress the copper sulfide while floating the molybdenite content of the concentrate. The use of sulfides with or without a collector for the molybdenum sulfide has been known and used in the industry for many years. However, in the last 25 years a process widely used in industry for differential flotation of molybdenite has included conditioning an aqueous pulp of the molybdenite-containing copper ore concentrate with a material known as a "Nokes-type" reagent for depressing the copper sulfide and with a conventional collector for molybdenum sulfide. The conditioned pulp is then subjected to froth flotation with a conventional flotation machine to obtain a molybdenum concentrate as the flotation overflow and a copper concentrate tailing as the flotation underflow.

Nokes-type reagents are complex sulfur compounds of phosphorus, arsenic or antimony and a caustic. See, in

this regard, Nokes et al U.S. Patent No. 2,492,936. They are substantially more expensive than simpler sulfides, for example, sodium hydrosulfide, costing at present about 1.5 times as much as such simple sulfides, but their effectiveness is such that substantially less Nokes-type reagent need be used than the simple sulfide with the result that the Nokes-type depressants have become a standard in the industry.

10           Although Nokes-type depressants are used at lower levels than the simple sulfides, their cost and constant consumption adds significantly to the cost of the molybdenum ultimately produced. An attempt to mitigate such costs can be found in Delaney U.S. Patent No. 3,655,044 wherein a process is described in which the amount of Nokes-type reagent required as a depressant is reduced so that only about one-fifth to one-half of the usual amount is needed. The process requires the addition of a collector for the molybdenum sulfide along with the use of an inert gas, such as nitrogen, as the froth producing gas. While ordinary  
20           collectors are not a major cost item, the use of nitrogen is sufficiently costly so that the aforementioned reduction in the concentration of Nokes reagent cannot readily justify nitrogen aeration, particularly when one considers that an increased capital investment may be required.

          The present invention provides a process for froth flotation of molybdenum sulfide which also employs nitrogen as the aerating gas but which is economically

1 operational because it (a) uses a depressant reagent for  
2 the copper sulfide which is substantially less costly than  
3 the Nokes-type reagent, (b) surprisingly operates with an  
4 amount of depressant reagent which can be as little as  
5 1/20 or less of the amount of depressant usually required  
6 in the absence of nitrogen aeration, and (c) can often  
7 operate without the further addition of a collector for  
8 the molybdenite.

9  
10 More particularly, an aqueous pulp of copper  
11 concentrate containing both molybdenum sulfide and copper  
12 sulfide is conditioned with a depressant comprising, as  
13 its major constituent, a water-soluble ammonium, alkali  
14 metal or alkaline earth metal sulfide and the conditioned  
15 pulp is subjected to froth flotation in which an inert  
16 gas comprising nitrogen as its major component is employed  
17 as the froth producing medium. A molybdenum concentrate  
18 is recovered in the flotation overflow and a copper con-  
19 centrate is recovered in the flotation underflow without  
20 the occurrence of substantial oxidation in the conditioned  
21 aqueous pulp.

22  
23 The present process is particularly suitable  
24 for continuous operation wherein the sulfide concentration  
25 of the copper ore concentrate pulp is measured on a con-  
26 tinuous basis and the above sulfide depressant is added  
27 in an amount sufficient to maintain the measured sulfide  
28 concentration above a predetermined value sufficient to  
29 effectively depress the copper sulfide. In accordance  
30 with the present invention, a sulfide concentration as

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little as 0.1 pounds per ton of concentrate can be used to effect satisfactory separation of the molybdenite.

10 The present invention, therefore, provides a process (and preferably a continuous process) for the separation and recovery of molybdenum sulfide from copper ore concentrate containing both molybdenum sulfide and copper sulfide which comprises conditioning an aqueous pulp of the copper ore concentrate with a depressant for said copper sulfide comprising as the major depressant constituent 0.1 lb lb to 3.0 lbs. per ton of said concentrate of a water-soluble ammonium, alkali metal or alkaline earth metal sulfide, and subjecting the conditioned pulp to froth flotation in which an inert gas comprising nitrogen as its major component is employed as the froth producing medium to effect recovery of a molybdenum concentrate in the flotation overflow and recovery of a copper concentrate in the flotation underflow without the occurrence of substantial oxidation in the conditioned aqueous pulp.

#### BRIEF DESCRIPTION OF THE DRAWINGS

20 FIGURE 1 is a graph showing the change in sulfide concentrations at different initial levels, measured by means of an electrode with respect to time when the pulp is aerated with air and with nitrogen; and

FIGURE 2 is a graph which illustrates the relationship between the percentage of molybdenite recovered, copper sulfide recovered and sulfide concentration, with respect to time when the pulp is aerated with air in one example and with nitrogen in another example.

DETAILED DESCRIPTION

As above-described, conventional ore beneficiation operations on sulfidic copper ores, such as chalcopyrite, can result in the preparation of a copper ore concentrate that typically contains up to about 30 percent by weight copper and up to about 1 percent by weight molybdenum. In accordance with the present invention, molybdenite is separated from the copper sulfide concentrate by the addition of a sulfide depressant for the copper sulfide and  
10 froth flotation by aeration with nitrogen. A collector for the molybdenite need not be added, but is not precluded, and, for particular ores, it may be desirable. In such case, any conventional collector can be used, such as potassium xanthate, fuel oil, or sodium di-sec-butyl-di-thiophosphate. Additionally, any conventional frother



can be added such as pine oil or methyl isobutyl carbinol (MIBC) and a commercial form of MIBC as sold by the Shell Oil. Co. under the designation 1638, comprising 90% MIBC and 10% still bottoms. As a result of the copper circuit, the pulp is at a pH level of about 11-12 or higher.

The copper sulfide depressant comprises as the major depressant constituent a water-soluble ammonium, alkali metal or alkaline earth metal sulfide. The term sulfide is meant to include monosulfides, polysulfides, hydrosulfides and hydrated forms. Specific examples of the sulfide compounds include ammonium sulfide, ammonium hydrosulfide, lithium sulfide, lithium hydrosulfide, sodium monosulfide, sodium hydrosulfide, potassium monosulfide, potassium hydrosulfide, rubidium monosulfide, cesium monosulfide, calcium hydrosulfide, strontium hydrosulfide, barium hydrosulfide, water-soluble polysulfide forms thereof, hydrated forms thereof, and mixtures thereof. It is an important and surprising result of the present invention that the foregoing sulfides, most of which are readily and economically available, can be used in the present process in place of a Nokes reagent at levels which are only a fraction of the amount normally required of such sulfides. Thus, while the usual total amount (rougher and cleaner operations) of sodium hydrosulfide required for effective molybdenite separation is about 10-25 pounds per ton (PPT), a satisfactory separation can be obtained with the present process by the typical use of 0.5-1 PPT and as little as 0.1 PPT of the sulfide. A satisfactory range, depending on the source of ore, is about 0.1-3 PPT. Accordingly, as little as 1/20 or less of the normal amount of sulfide is required. Particularly preferred, economically

optimal sulfides are sodium sulfide, sodium hydrosulfide, ammonium sulfide, ammonium hydrosulfide and mixtures thereof.

The froth flotation is carried out in conventional agitator-equipped flotation cells which otherwise use air as the froth producing gas. In the present invention, nitrogen is used in place of air; more broadly, an inert gas is used which comprises nitrogen as its major component.

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Electrode determination of the concentration of sulfide in the pulp can be used as a measure of whether copper sulfide is being effectively depressed. Such electrodes are commercially available and can be exemplified by the "Orion"\* Research Model 94-16 electrode (Orion Research Incorporated, Cambridge, Massachusetts) which is specific for silver ion and for sulfide ion activity. The electrodes are periodically standardized using 0.10 molar sodium sulfide solution. An amplified millivolt signal is plotted automatically on a strip chart and represents the sulfide concentration. Any abrupt change in slope of the sulfide content, as measured on the strip chart, indicates a drop-off in depressant concentration. Referring to Figure 1, there is plotted the concentration of sulfide as indicated by millivolt reading from an "Orion" Research electrode in various pulp slurries. When 6.0 PPT, of sodium hydrogen sulfide is added to a copper sulfide concentrate pulp, and air is used for the froth flotation, there is a rapid drop in

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1 sulfide concentration, as indicated by the line 10. After  
2 3-4 minutes, the amount of sulfide concentration is so  
3 low that an inordinate amount of copper sulfide floats  
4 with the molybdenum sulfide. When nitrogen is substituted  
5 for air there is virtually no drop in sulfide concentration  
6 over the full 10 minutes of flotation, as indicated by the  
7 line 12. As shown by the line 14, when the amount of sodium  
8 hydrogen sulfide is reduced to 1/10 of the above amount,  
9 i.e., 0.6 PPT, the initial concentration of the sulfide is,  
10 of course, lower and there is some drop with time, but,  
11 importantly, the level is maintained at a sufficient con-  
12 centration to prevent inordinate copper floating.

13  
14 In a further embodiment, the present invention  
15 is particularly suitable for a continuous process in which  
16 concentrate pulp is fed on a continuous basis to a bank  
17 of serially disposed froth flotation cells. The floated  
18 froth, i.e., the molybdenum rougher concentrate, can be  
19 reslurried for one or more successive operations and  
20 sulfide depressant is preferably added as needed to each  
21 cleaner bank of cells. In accordance with this embodiment,  
22 the quantity of reagent used is regulated by the concen-  
23 tration of sulfide ion which is measured on a continuous  
24 basis as an amplified millivolt signal given by an elec-  
25 trode, as above described. The phrase "continuous basis"  
26 is meant to include measurements which are either contin-  
27 uous without interruption or are periodic. While it is  
28 preferred to measure the sulfide concentration without  
29 interruption, periodic measurements are satisfactory if  
30 the intervals are short enough so that quality control can

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be maintained. By continuous monitoring of the sulfide content and adjustment thereto to the level desired, e.g. 0.1 PPT of NaHS, a minimum amount of sulfide can be used to obtain a satisfactory depression of the copper sulfide. Taken together with the lower sulfide addition permitted by the use of nitrogen as the aerating gas, the total savings are quite substantial.

10 In order that those skilled in the art may better understand how the present invention may be practiced, the following Examples are given by way of illustration and without limitation.

#### EXAMPLE I

20 A pulp charge of 1343 grams of copper sulfide concentrate obtained from rougher and cleaning floatation of Pima Arizona chalcopryite, and containing 24.3% copper and 1.0% molybdenum, was added to a standard laboratory flotation machine, sold under the trade mark "Agitair", and diluted with 4 liters of water. Sufficient sodium hydrosulfide was added to obtain a concentration of 8 pounds of the sulfide per ton of the concentrate. The sulfide ion concentration was monitored with an "Orion" Research Sulfide Ion electrode. The pulp was allowed to condition until stable sulfide ion readings were obtained on a strip chart. At that point, air was injected and flotation carried out for a period of 16 minutes. During the flotation, the voltage output from the sulfide ion electrode was continuously recorded on a strip chart

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recorder. The flotation overflow, i.e., the froth, was collected at 2 minutes intervals, the mineral content thereof was weighed and the copper and molybdenum content were assayed. At the conclusion of the run, the flotation underflow was collected, the mineral content thereof was weighed and the copper and molybdenum content were assayed. The results are set forth in Table I.

TABLE I

Time, Min.	Wt. mineral Rec.	Assay		Cum. weight		Recovered	
		% Cu	% Mo	Cu	Mo	% Cu	% Mo
2	60.7	10.26	16.74	6.23	10.16	1.91	74.59
4	23.9	16.56	7.83	10.18	12.03	3.12	88.32
6	18.7	22.25	3.50	14.34	12.68	4.39	93.09
8	19.1	25.40	1.11	19.19	12.89	5.88	94.63
10	30.0	25.91	0.555	26.97	13.06	8.27	95.88
12	147.5	31.90	0.182	74.0	13.33	22.7	97.85
14	196.9	30.99	0.047	135	13.42	41.41	98.52
16	181.3	29.01	0.023	188	13.47	57.67	98.89
tails	665	20.73	0.023	326	13.62		

EXAMPLE II

The procedure of Example I was followed in all details except that sodium hydrosulfide was used in a concentration of 1 PPT and pure nitrogen was used in place of air as the aeration gas. The pulp charge was 1353 grams of copper sulfide concentrate containing 25.0% copper and 0.97%

molybdenum. Measurements, weighings and assays were conducted as in Example I. The results are set forth in Table II.

TABLE II

<u>Time,</u> <u>Min.</u>	<u>Wt. mineral</u> <u>Rec.</u>	<u>Assay</u>		<u>Cum. weight</u>		<u>Recovered</u>	
		<u>% Cu</u>	<u>% Mo</u>	<u>Cu</u>	<u>Mo</u>	<u>% Cu</u>	<u>% Mo</u>
2	62.4	27.94	16.47	17.43	10.27	5.15	78.0
4	19.6	13.51	7.94	20.08	11.83	5.92	90.0
6	15.4	19.00	2.956	23.01	12.29	6.8	93.2
8	14.5	23.52	2.120	26.41	12.59	7.8	95.5
10	15.4	26.11	1.229	30.43	12.78	9.0	97.0
12	14.8	26.62	0.792	34.38	12.90	10.1	98.5
14	10.4	26.62	0.582	37.15	12.96	10.8	98.6
16	11.3	26.62	0.419	40.15	13.01	11.8	98.8
tails	1189	25.10	0.014	338.5	13.18		

A comparison of the results in Tables I and II reveals that not only was a greater percentage of molybdenum recovered in a shorter period of time but containing very much less copper, all with the use of, in this case, 1/8 the amount of sodium hydrosulfide.

Referring to Figure 2, the results listed in Tables I and II are shown graphically along with the sulfide ion concentration as represented by the millivolt reading from an "Orion" Research electrode in each case. The solid line indicates the values pertinent to the first Example and the dashed line indicates the values pertinent to the second Example. It can be seen that a slight benefit was obtained in terms of molybdenum recovery and that a tremendous benefit

was obtained with respect to the continued depression of copper sulfide.

EXAMPLES III-XIV

The procedure of Example II can be followed except that in twelve separate runs, 1 PPT of ammonium sulfide, ammonium hydrosulfide, lithium sulfide, lithium hydrosulfide, sodium monosulfide, potassium monosulfide, potassium hydrosulfide, rubidium monosulfide, cesium monosulfide, calcium hydrosulfide, strontium hydrosulfide and barium hydrosulfide, respectively, are substituted for the sodium hydrosulfide.

It should be understood that while the present invention has been described in considerable detail with respect to certain specific embodiments thereof, it is not to be considered limited to those embodiments, but may be used in other ways which do not depart from the spirit of the invention or the scope of the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for the separation and recovery of molybdenum sulfide from copper ore concentrate containing both molybdenum sulfide and copper sulfide which comprises conditioning an aqueous pulp of the copper ore concentrate with a depressant for said copper sulfide comprising as the major depressant constituent 0.1 lb lb to 3.0 lbs. per ton of said concentrate of a water-soluble ammonium, alkali metal or alkaline earth metal sulfide, and subjecting the conditioned pulp to froth flotation in which an inert gas comprising nitrogen as its major component is employed as the froth producing medium to effect recovery of a molybdenum concentrate in the flotation overflow and recovery of a copper concentrate in the flotation underflow without the occurrence of substantial oxidation in the conditioned aqueous pulp.

2. The process according to Claim 1 in which said non-oxidizing aerating gas consists essentially of nitrogen.

3. The process according to Claim 1 in which said sulfide is selected from the group consisting essentially of sodium sulfide, sodium hydrosulfide, ammonium sulfide, ammonium hydrosulfide, and mixtures thereof.

4. The process according to Claim 1 in which said water soluble depressant consists essentially of said sulfide.

5. A continuous process for the separation and recovery of molybdenum sulfide from copper ore concentrate containing both molybdenum sulfide and copper sulfide, which comprises measuring on a continuous basis the sulfide concentration of an aqueous pulp of the copper ore concentrate, adding to said aqueous pulp a depressant for said copper sulfide comprising as the major depressant constituent 0.1 to



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3.0 lbs per ton of said concentrate of a water-soluble ammonium, alkali metal or alkaline earth metal sulfide and subjecting the conditioned pulp to froth flotation in which an inert gas comprising nitrogen as its major component is employed as the froth producing medium to effect recovery of a molybdenum concentrate in the flotation overflow and recovery of a copper concentrate in the flotation underflow without the occurrence of substantial oxidation in the conditioned aqueous pulp.

6. The process according to Claim 5 in which said non-oxidizing aerating gas consists essentially of nitrogen.

7. The process according to Claim 5 in which said sulfide is selected from the group consisting essentially of sodium sulfide, sodium hydrosulfide, ammonium sulfide, ammonium hydrosulfide, and mixtures thereof.

8. The process according to Claim 5 in which said water soluble depressant consists essentially of said sulfide.



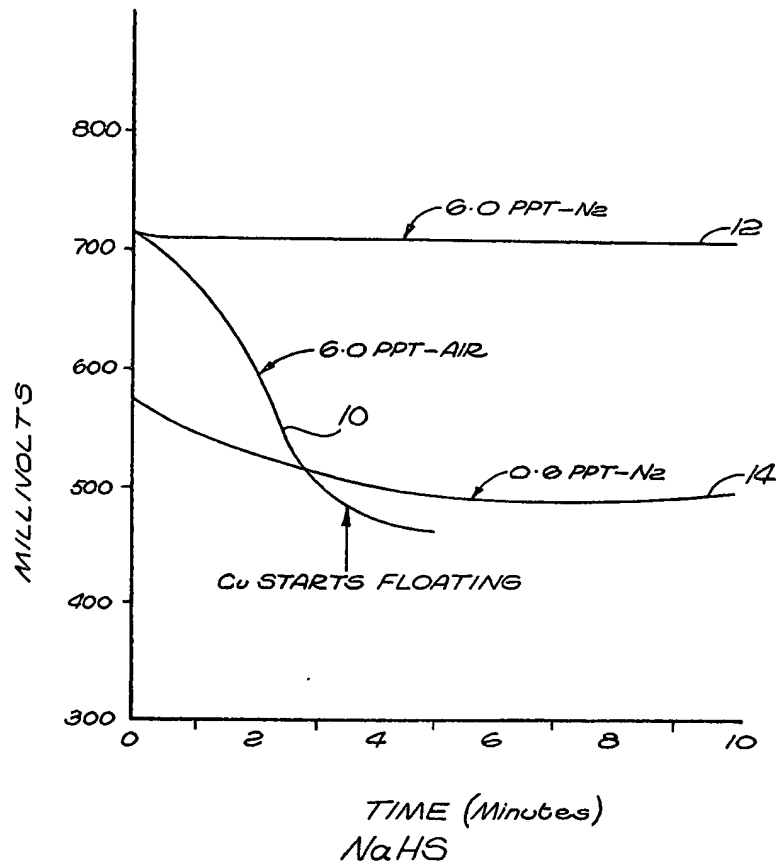
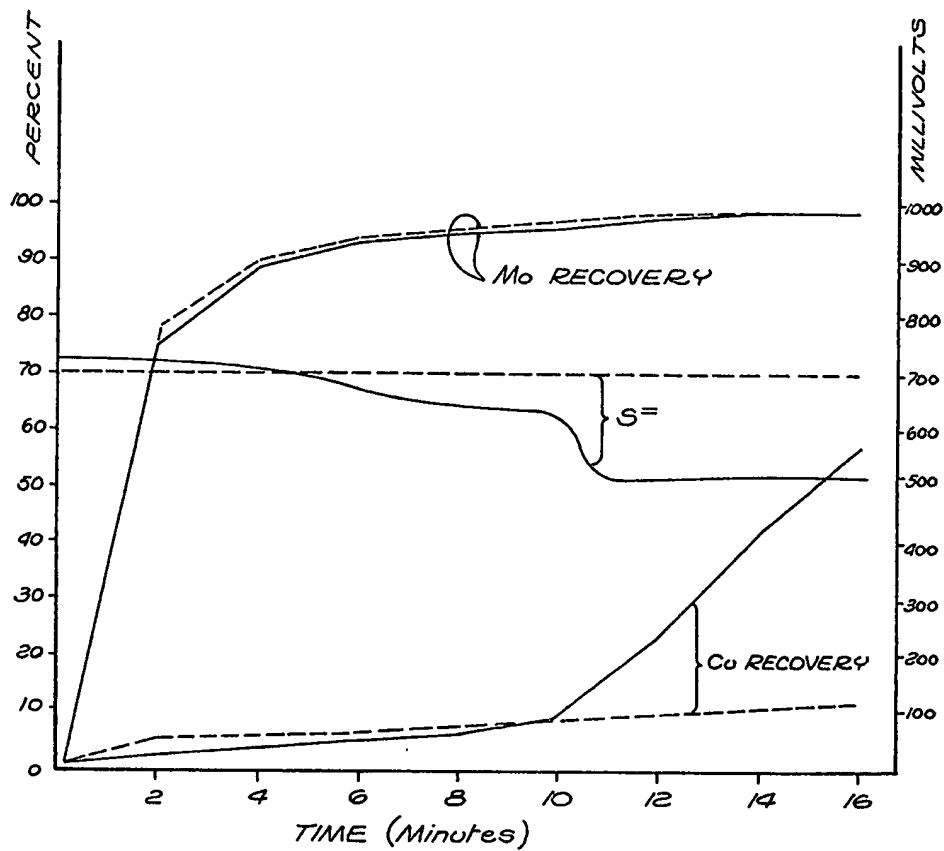


FIG.1.

3-2



LEGEND:-  
—— 8 PPT NaHS, FLOAT W/AIR  
----- 1 PPT NaHS, FLOAT W/N<sub>2</sub>

FIG. 2.

*Gowling & Henderson.*

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